SUPPORTING INFORMATION

Addition of H_2O and O_2 to Acetone and Dimethylsulfoxide Ligated Uranyl(V) Dioxocations

Christopher M. Leavitt[1], Vyacheslav S. Bryantsev[2], Wibe A. de Jong[3], Mamadou S. Diallo[2], William A. Goddard III[2], Gary S. Groenewold[4*] and Michael J. Van Stipdonk[1*]

[1]Department of Chemistry
Wichita State University
Wichita, KS

[2]Materials and Process Simulation Centre, Beckman Institute 139-74
California Institute of Technology
Pasadena, CA

[3]William R. Wiley Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
Richland, WA

[4]Interfacial Chemistry Group
Idaho National Laboratory
Idaho Falls, ID

Figure S1 shows mass spectra generated by isolation of (a) $[UO_2(aco)(H_2O)]^+$, (b) $[UO_2(dmso)(H_2O)]^+$, (c) $[UO_2(aco)(O_2)]^+$ and (d) $[UO_2(dmso)(O_2)]^+$ derived from isolation and storage of $[UO_2(lig)]^+$ in the ion trap mass spectrometer. Table 1S shows the effect of the basis set size on binding energies, Table 2S and Table 3S list electronic binding energies, geometric parameters and frequencies for **1–12** calculated at the B3LYP/SSC/6-311++G** level of theory, Cartesian coordinates and energies (Hartrees) for the M06-L/SSC/6-311++G** optimized geometries.

Figure S1 – Isolation of (a) $[UO_2(aco)(H_2O)]^+$, (b) $[UO_2(dmso)(H_2O)]^+$, (c) $[UO_2(aco)(O_2)]^+$ and (d) $[UO_2(dmso)(O_2)]^+$ from isolation of $[UO_2(lig)]^+$ (MS^3).

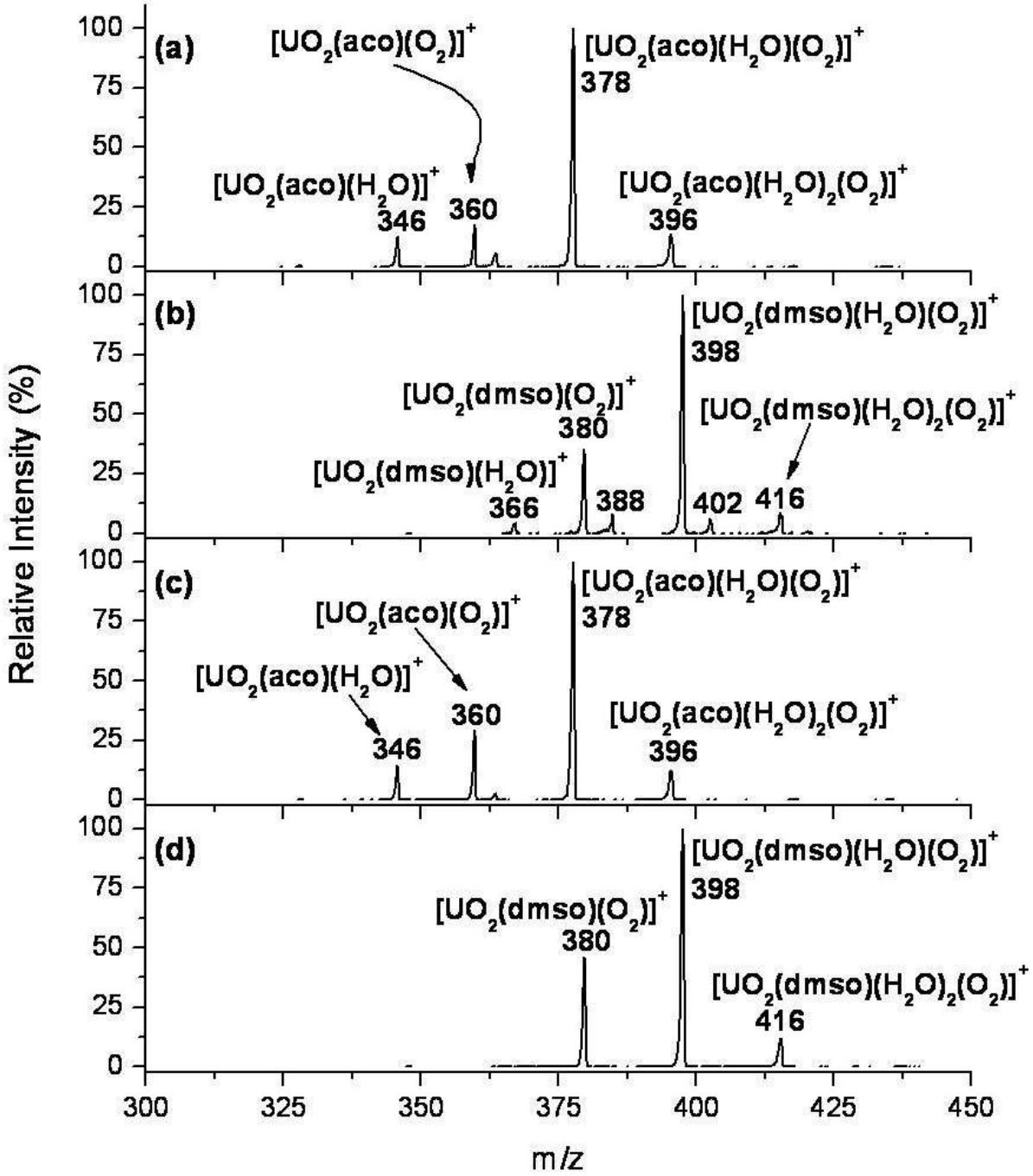

Table 1S. The effect of the basis set size on B3LYP binding energies of water and dioxygen to U(V) compounds (kcal/mol)

basis set	$UO_2^+ + H_2O$	$UO_2^+ + O_2$	$[UO_2(dmso)]^+ + O_2$
SSC /6-311++G**	-35.97	-15.42	-23.90
SSC(2g)/6-311++G(3df,3pd)[a]	-34.31	-19.44	-27.04
SSC(3g,1h)/aug-cc-pVTZ	-34.35	-19.77	-27.18

[a]Single point energies on B3LYP/ SSC /6-311++G** optimized geometries.

Table 2S. B3LYP binding energies (kcal/mol) of acetone, dimethylsulfoxide , water , and dioxygen to U(V) compounds[a]

reaction	lig=aco	lig=dmso
$UO_2^+ + lig$	-46.35	-56.56
$[UO_2(lig)]^+ + H_2O$	-28.11	-27.08
$[UO_2(lig)(H_2O)]^+ + H_2O$	-24.48	-23.49
$[UO_2(lig)]^+ + O_2$	-25.63	-27.04
$[UO_2(lig)(H_2O)]^+ + O_2$	-27.59	-28.75
$[UO_2(lig)(H_2O)_2]^+ + O_2$	-26.63	-27.80
$[UO_2(lig)(O)_2]^+ + H_2O$	-30.06	-28.79
$[UO_2(lig)(H_2O)(O)_2]^+ + H_2O$	-23.52	-22.54

[a]B3LYP/SSC(2g)/6-311++G(3dp,3df) single point energies on B3LYP/SSC/6-311++G** optimized geometries.

Table 3S. B3LYP optimized distances[a] (Å), asymmetric (ν_a) and symmetric (ν_s) O=U=O stretching frequencies in complexes **1**-**12**[a]

system	U=O	U···aco/dmso	U···H_2O	U···O_2[c]	O–O	ν_a, cm^{-1}	ν_s, cm^{-1}
1	1.779	2.361				960.5	882.2
2	1.792	2.391	2.508			935.8	869.9
3	1.792	2.404	2.514			919.0	857.8
4	1.752	2.318		2.313, 2.322	1.298	1007.3	917.9
5	1.761	2.353	2.503	2.341, 2.331	1.300	989.9	901.6
6	1.768	2.397	2.525, 2.524[b]	2.350, 2.354	1.300	976.4	889.3
7	1.783, 1.789	2.300				943.5	868.0
8	1.795, 1.804	2.328	2.512			920.5	848.8
9	1.794, 1.807	2.354	2.519, 2.523			903.1	835.5
10	1.756, 1.760	2.248		2.316, 2.334	1.300	993.4	891.7
11	1.764, 1.769	2.279	2.510	2.346, 2.341	1.301	977.8	881.5
12	1.772, 1.773	2.311	2.533, 2.524[b]	2.360, 2.371	1.303	967.0	874.8

[a]Obtained with B3LYP/SSC/6-311++G**. [b]The H_2O ligand trans to the O_2 ligand. [c]The bond adjacent to the ACO/DMSO ligand is listed first.

Cartesian coordinates and energies (Hartrees) for the M06-L/SSC/6-311++G** optimized geometries

1, $[UO^2(aco)]^+$ E = -820.591239

U	-0.00453895	-0.00631931	0.85562346
O	-0.00443761	-1.77452829	0.80529210
O	-0.02364609	1.75694620	1.00651374
O	0.03939584	0.05134282	-1.51824256
C	0.02685352	0.01852061	-2.75831579
C	1.29161502	0.08887522	-3.52720093
H	1.28368128	-0.62633673	-4.35281645
H	1.35288935	1.07976023	-3.99234816
C	-1.25322545	-0.09661169	-3.49693809
H	-1.25167207	0.53401393	-4.38814137
H	-2.11389185	0.12459661	-2.86963727
H	2.16684916	-0.05848775	-2.89874270
H	-1.34045475	-1.12812032	-3.85905259

2, $[UO_2(aco)(H_2O)]^+$ E = -897.079202

U	0.46325197	0.15776612	0.53621866
O	1.14127777	-1.48496793	0.63856925
O	-0.19794710	1.81122555	0.55176030
O	-0.76636840	-0.40240145	-1.45883241
C	-1.34765443	-0.65036479	-2.52133029
C	-0.72312655	-0.31882140	-3.82739458
H	-1.45873875	0.09773581	-4.51872517
H	0.12365168	0.35535315	-3.71883286

H	-0.37399649	-1.25117545	-4.28596301
C	-2.68801546	-1.28945892	-2.52046821
H	-3.43018200	-0.53000559	-2.79192579
H	-2.75316822	-2.06001323	-3.29177062
H	-2.94497787	-1.69922960	-1.54627614
O	-0.97316847	-0.40913318	2.52670825
H	-1.59862122	0.17433328	2.97005070
H	-0.97647122	-1.24160839	3.01169279

3, $[UO_2(aco)(H_2O)_2]^+$ E = -973.564230

U	0.53545278	-0.30338292	0.00061399
O	0.58520481	-0.34034480	1.78146549
O	0.59418504	-0.32788151	-1.78018156
O	-1.56967968	0.88936778	-0.00081075
C	-2.64314334	1.49760040	-0.00145875
C	-2.67711896	2.98345930	0.01390687
C	-3.93518382	0.76306883	-0.01769502
H	-1.70855365	3.41611414	-0.22671256
H	-3.80876666	-0.29000297	0.22368847
H	-3.44658082	3.36419208	-0.66104833
H	-2.96839248	3.30952512	1.01879986
H	-4.65795518	1.22784919	0.65622801
H	-4.36354189	0.84472863	-1.02308592
O	2.71499969	0.96984085	0.00707391
H	3.21369167	1.25230205	-0.76699834
H	3.21505655	1.24993925	0.78110406
O	0.56354611	-2.82741849	-0.00457914

H	0.58091492	-3.40038859	-0.77855446
H	0.57696544	-3.40032164	0.76954503

4, $[UO_2(aco)(O_2)]^+$ E = -970.987794

U	0.52535150	0.25004284	-0.51129783
O	1.33641841	-1.29903643	-0.48769535
O	-0.13810248	1.86783141	-0.50429691
O	-0.41159167	-0.17831104	1.57831409
C	-1.14813050	-0.55066929	2.50977606
C	-2.47055586	-1.15090861	2.22563532
H	-2.67894629	-1.97704598	2.90846827
H	-3.23335418	-0.39031627	2.43400615
C	-0.70697471	-0.38945656	3.91221789
H	-1.53297118	-0.04820984	4.54016163
H	0.15088282	0.27252805	4.00291649
O	-1.47866074	-0.68881887	-1.27689613
O	-0.81752808	-0.38575473	-2.33597248
H	-2.57063097	-1.46660502	1.18941447
H	-0.43205616	-1.38006899	4.29452707

5, $[UO_2(aco)(H_2O)(O_2)]^+$ E = -1047.479263

U	0.62906287	-0.00075496	0.07993543
O	0.67289893	1.75571434	0.10634006
O	1.98379237	0.07815450	2.19826433
O	0.66389011	-1.75142587	0.22528883
O	-1.71859414	0.01564800	0.35761708
C	-2.93563994	0.02116203	0.11638464

C	-3.91462641	0.00309133	1.22848614
H	-4.74273635	0.68632009	1.02784952
H	-4.35763318	-0.99877903	1.27356803
H	-3.45137599	0.22531755	2.18686832
C	-3.43151456	0.04698043	-1.28005090
H	-3.79916160	1.05905773	-1.48801624
H	-4.29285082	-0.61355636	-1.39984391
H	-2.65392261	-0.19490993	-2.00112449
O	1.34461822	-0.07971456	-2.17115426
O	0.05958125	-0.07839431	-2.21908900
H	2.30889267	0.87186329	2.63934194
H	2.31556142	-0.67462153	2.70166049

6, $[UO_2(aco)(H_2O)_2(O_2)]^+$ E = -1123.963613

U	0.26365303	0.45041157	0.00393303
O	0.36623994	0.44263600	1.76568549
O	0.35153097	0.50174697	-1.75776247
O	-0.38604113	-1.86987961	-0.02834440
O	2.69222116	-0.25569456	-0.01572326
O	-1.67001620	1.83915508	0.03385648
O	1.17954419	2.81488833	0.03627067
C	-1.14418955	-2.84774027	-0.02665144
O	-2.10758369	0.62723900	0.00797960
C	-2.61854478	-2.67794671	0.01689078
H	-2.99494736	-2.77513767	-1.00879093
H	-3.09243452	-3.47509212	0.59199573
H	-2.91036067	-1.69980767	0.39249992

C	-0.58736046	-4.22262957	-0.07871593
H	-1.15262005	-4.84081594	-0.78015455
H	0.47119645	-4.22568303	-0.32755904
H	-0.72445638	-4.68581586	0.90498283
H	3.24844838	-0.42001896	0.75325390
H	3.24409675	-0.39340248	-0.79301737
H	1.16927462	3.38097460	0.81594107
H	1.15674505	3.40489507	-0.72520286

7, $[UO_2(dmso)]^+$ E = -1180.645945

O	0.02589261	-0.03166762	1.33257227
S	-0.70845955	0.34977639	2.64990246
C	-2.40253403	-0.20379900	2.40572679
H	-2.94926532	-0.04664207	3.33679036
H	-2.83709796	0.41081782	1.61801036
C	-0.15161451	-0.90000414	3.81342319
H	-0.70115605	-0.76356336	4.74597922
H	0.91040764	-0.73304563	3.98597656
H	-2.40973037	-1.25762300	2.12527598
H	-0.32536224	-1.89189214	3.39635958
U	0.25398353	0.02524157	-0.97313315
O	1.95932047	-0.45820655	-0.97252086
O	-1.45799694	0.49072471	-1.12168150

8, $[UO_2(dmso)(H_2O)]^+$ E = -1257.131920

O	0.04698860	-0.29404678	1.45848689
S	-0.73393973	0.15991842	2.72021704

C	-2.43248985	-0.35423122	2.41976214
H	-3.02320238	-0.12871849	3.30882421
H	-2.80124792	0.22629327	1.57443024
C	-0.27460375	-1.06324118	3.95391584
H	-0.86585146	-0.88250176	4.85268099
H	0.78221587	-0.92156458	4.17403061
H	-2.45845836	-1.42169531	2.19757694
H	-0.45446626	-2.06285790	3.55832639
U	0.23177395	-0.08604671	-0.87479284
O	1.91381547	-0.67115153	-0.97240582
O	-1.43813661	0.56623302	-0.91595788
O	1.09221322	2.14049484	-1.70076586
H	2.01352775	2.34134731	-1.89860101
H	0.58192678	2.92547097	-1.92662075

9, $[UO_2(dmso)(H_2O)_2]^+$ E = -1333.614575

O	0.17224149	-0.17642733	1.64751814
S	-0.71536870	0.28771503	2.83077504
C	-2.38141157	-0.25229734	2.41309739
H	-3.04385719	-0.00503099	3.24385028
H	-2.67663867	0.29812543	1.51970119
C	-0.34270809	-0.90592343	4.12222055
H	-1.01059016	-0.72094293	4.96463657
H	0.68962421	-0.74375571	4.42756946
H	-2.38080718	-1.32651518	2.22337516
H	-0.47251996	-1.91486458	3.73071334
U	0.26905535	0.06031504	-0.70878304

O	1.92681194	-0.57697062	-0.91229951
O	-1.40564140	0.71473663	-0.63471709
O	1.05170836	2.29543287	-1.61206941
H	1.95981825	2.51551502	-1.84519712
H	0.51913129	3.07607671	-1.79566329
O	-0.39022129	-1.88319843	-2.20532111
H	0.25072513	-2.52249948	-2.53449049
H	-1.24096171	-2.11734323	-2.58965420

10, $[UO_2(dmso)(O_2)]^+$ E = -1331.045919

O	0.16585356	0.66558261	1.33478536
S	-0.59468311	0.68615413	2.69774437
C	-2.25696810	0.12944978	2.29504502
H	-2.81241429	0.04125494	3.23035754
H	-2.71756870	0.89367514	1.67002201
C	0.02416298	-0.78098330	3.52956775
H	-0.52809497	-0.89389364	4.46388293
H	1.07783561	-0.61094931	3.74580128
H	-2.21133317	-0.82859658	1.77554065
H	-0.10896491	-1.65019673	2.88496088
U	0.30435919	0.20124289	-0.87300678
O	2.01271473	-0.17450106	-0.80209476
O	-1.37464997	0.67186290	-1.08758117
O	-0.32251303	-1.90490905	-0.04629094
O	-0.25917491	-2.05002747	-1.32448450

11, $[UO_2(dmso)(H_2O)(O_2)]^+$ E = -1407.535615

O	0.23026345	0.76663579	1.45287298
S	-0.53283176	0.94068437	2.79675809
C	-2.21963008	0.42677591	2.43571326
H	-2.78004687	0.42931602	3.37202525
H	-2.64721425	1.15840589	1.75134894
C	0.00168192	-0.47568147	3.76681812
H	-0.55662756	-0.47254935	4.70420894
H	1.06296491	-0.34466591	3.97247099
H	-2.21288747	-0.56780272	1.98743618
H	-0.17691820	-1.39273125	3.20506938
U	0.26834877	-0.02936712	-0.69513047
O	1.95960074	-0.50481807	-0.60950785
O	-1.38440538	0.53682331	-0.94548973
O	-0.48783493	-1.96479589	0.45759504
O	-0.47320289	-2.28686147	-0.79023725
O	1.03108141	1.72138792	-2.34193066
H	1.94327142	1.86611253	-2.61906811
H	0.49058423	2.35732938	-2.82426901

12, $[UO_2(dmso)(H_2O)_2(O_2)]^+$ E = -1484.018479

O	-0.35213160	0.53054258	1.68080511
S	-0.98743148	0.00594685	2.98999053
C	-2.61070211	-0.59854434	2.49643688
H	-3.08810774	-1.04086269	3.37221508
H	-3.18706895	0.26342057	2.16274333
C	-0.17381390	-1.57294188	3.28874474
H	-0.62523883	-2.02481362	4.17337578

H	0.87700230	-1.36150571	3.48286479
H	-2.50340998	-1.33037855	1.69564155
H	-0.28797752	-2.21695240	2.41660071
U	0.27241526	0.23122454	-0.54465048
O	1.87837932	-0.35606399	-0.09376396
O	-1.24336488	0.91714289	-1.14362623
O	-0.76340964	-1.84328942	0.02344393
O	-0.39963239	-1.96915110	-1.21012014
O	1.02456445	0.08645315	-2.96529014
H	1.79528898	-0.40790635	-3.26419360
H	0.43050274	0.14784152	-3.72098773
O	1.23042650	2.57022267	-0.56533475
H	2.11681039	2.82869531	-0.29166732
H	0.74871198	3.38330668	-0.75039411